Investigating the synergistic effects in tourmaline/TiO₂-based heterogeneous photocatalysis: Underlying mechanism insights

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ABSTRACT

We proposed to combine a polarized mineral tourmaline and TiO₂ nanosemiconductor to form a hybrid photocatalyst, to simultaneously optimize the photocatalytic efficiency and macroscopic aggregation of nano-TiO₂. Photoactivity assessment toward bisphenol A (BPA) degradation indicated the optimal T(20%)-TiO₂ catalyst exhibited higher performance than the bare TiO₂ or the mechanical mixtures. In view of the reactive species scavenging results and intermediate identification, a hydroxyl radical-initiated oxidation as the dominating BPA decomposition pathway was proposed. The results of photoluminescence spectra and photocurrent measurements along with electrochemical impedance spectra and Mott–Schottky analyses led us to a better understanding of the photocatalytic process involving the facilitated charge transfer and higher carrier density induced owing to tourmaline incorporation. The synergistic effects in tourmaline-involved photocatalysis would be attributed to the fact that the internal dipolar field, originating from tourmaline spontaneous polarization, resulted in spatially varied energy levels of the bands and changed band bending of TiO₂ semiconductor, which lowered the potential barrier for photoelectrons or holes to readily migrate to the surface and retarded electron–hole recombination. The concept of engineering internal field in heterogeneous photocatalysis using a polarized mineral of low cost will shed new light on applied photochemistry and development of nanotechnology enabled approaches for water treatment.

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1. Introduction

TiO₂-based heterogeneous photocatalysis has gained far-reaching importance due to its strong photoreactivity, economic viability, non-toxicity and photostability [1], and has been widely used for pollution abatement. Generally, TiO₂ mediated photocatalysis is initiated by the absorption of photons with sufficient energy relative to the band gap ($h\nu \geq E_g$), which results in charge separation with electrons promotion from the valence band (VB) to the conduction band (CB). The photogenerated electron–hole pairs can undergo recombination, get trapped in metastable states, or migrate to the surface and initiate redox reactions [2]. Because of the ineffective electron transfer and rapid recombination between

the charge carriers, however, the quantum efficiency is inherently low for most TiO₂ mediated photocatalysis. It is also noticeable that nanoscale size effects often come at the expense of the rapid recombination rate of the electron–hole pairs for restricted spatial proximity [3,4]. Yet, new directions are required to promote the quantum efficiency, which have inspired to extensive research efforts.

One strategy toward mitigating catalyst efficiency decrease from recombination is to utilize internal electric fields. In the presence of internal electric fields, the promoted motion of photogenerated charge carriers toward opposite directions and even the spatial separation of redox sites can be achieved [5], and band bending can be manipulated as well, for electron–hole pairs separating. Internal electric fields within photocatalysts can be associated with ferroelectric polarization [6,7], and electrochemical potential differences across phase boundaries which could be engineered in *p–n* junctions, polar surface terminations and

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polymorph junctions [8–11]. Recently, some reports focused on the polarizable semiconductors (e.g., ferroelectrics, such as LiNbO_3 [12], BiFeO_3 [13]) to improve photocatalytic activity. Moreover, the influence of ferroelectric polarization on photogenerated charge carriers and photochemical reactions can also extend to the supported non-ferroelectric coating [14–17]. This concept provides an innovative alternative for photocatalyst design with better performance. However, the reduction of TiO_2 or/and ferroelectric particle size will bring about new problems such as catalyst agglomeration and difficult recovery, which limit the practical application of TiO_2 , in spite of its large surface areas. Hence, in this work, to simultaneously optimize photocatalytic efficiency, nanoparticle aggregation and recovery, a method of immobilization of TiO_2 onto polarized tourmaline was proposed to approach the goal of mineral-induced spontaneous polarization assisted photocatalysis, which could indeed provide a promising alternative for cost-effective environmental application due to the environmentally benign nature, chemical inertia, low cost and ubiquity of tourmaline in the natural environment.

Tourmaline, distributed in different geologic environments, is categorized into a complex class of borosilicate with space group of $R3m$ (C_{3v}^5). The chemical compositions can be expressed by the general formula $\text{XY}_3\text{Z}_6\text{T}_6\text{O}_{18}(\text{BO}_3)_3\text{V}_3\text{W}$. Its crystal structure contains hexagonal rings of corner-shared Si–O tetrahedra. The edge-sharing Y- and Z-octahedra bridging each tetrahedral ring are formed by Y cation (e.g., Li^+ , Mg^{2+} , Fe^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Mn^{3+} , or Cr^{3+}) and Z cation (e.g., Al^{3+} , Fe^{3+} , Cr^{3+} , V^{3+} , Mg^{2+}), respectively. The X-site is often occupied by Na^+ , K^+ , Ca^{2+} , or vacancy. With dominant occupancy of Si, possible substitution by boron can also occur on the T-site. The V- and W-sites are occupied by OH^- , O^{2-} , and OH^- , O^{2-} , F^- , respectively [18]. Tourmaline has fascinating properties analogous to ferroelectrics and exhibits a unique behavior with spontaneous and permanent poles, different from any other minerals in natural geologic environment. Internal dipolar field presents in the vicinity of the surface of micron-sized tourmaline with an intensity of 10^6 – 10^7 V/m, which arises from the spontaneous polarization due to lack of symmetric center, mirror plane, or rotation axes oriented perpendicular to the c axis in the crystal [19]. In this sense, incorporation of TiO_2 to a polarizable mineral, tourmaline, can be envisioned to meet the challenges of both quantum efficiency and nanoparticles aggregation in TiO_2 -based photocatalysis. However, the limited assessments concerned to date [20–22] mainly concentrated on parameter optimization and kinetic analysis of the degradation process. Only Yeredla and Xu [19] attempted to explain the mechanism for the enhanced activity in photosplitting of water at the band bending level; nevertheless, the results obtained were highly speculative for deficiency in supportive data and characterization means available. As such, current researches are often subject to the poor interpretation for the synergistic effect as well as the ambiguous role of tourmaline, the relevant exploration with a deep investigation into the mechanism and experimental parameters is still insufficient.

In the present study, the synthesis, characterization and preliminary photoactivity evaluation of nanosized TiO_2 supported on tourmaline were performed with the aim to retard electron–hole recombination and to overcome nanoparticles aggregation. Bisphenol A (BPA) was chosen as a model pollutant for its ubiquity in aquatic environment and endocrine-disrupting properties associated with various adverse health effects. The tourmaline/ TiO_2 -based heterogeneous photocatalysis was evaluated in terms of the extent of BPA degradation, and the impacts of coexisting substances. Furthermore, intermediate products of BPA degradation were identified, and for the first time, the mechanism of the tourmaline-involved photocatalysis was proposed with emphases on the charge-transfer process and the energy level

associated with band bending of TiO_2 based on the investigation of the photoluminescence spectra and photocurrent measurements along with the electrochemical impedance spectra and Mott–Schottky analyses.

2. Experimental

2.1. Reagents and materials

BPA was supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). N,O -Bis(trimethylsilyl) trifluoroacetamide with 1% of trimethylchlorosilane as the catalyst (BSTFA+TMCS, 99:1) was purchased from Regis Technologies, Inc. (Morton Grove, IL, USA). Methanol (J.T. Baker), acetonitrile and dichloromethane (Concord Technology Co., Ltd.), t -butanol (Guangfu Fine Chemical Research Institute), n -hexane (CNW Technologies GmbH) were all of high performance liquid chromatography (HPLC) grade and were used as received. All other chemicals were of analytical grade without any purification.

Tourmaline was provided by Lingshou Minerals Processing Co., Ltd., Hebei, China. Its chemical composition (wt.%) was as follows: SiO_2 , 37.44%; Al_2O_3 , 29.79%; Fe_2O_3 , 20.2%; CaO , 0.71%; Na_2O , 2.18%; MgO , 0.55%; K_2O , 0.14%; TiO_2 , 0.49%; B_2O_3 , 0.78%, and others 7.72%.

2.2. Materials synthesis and characterization

Tourmaline/ TiO_2 nanocomposites were prepared by a typical sol–gel method (Supplementary information). Generally, the catalysts were obtained through thermal treatment (80°C for 12 h, 120°C for 2 h) and then calcination (400°C for 3 h) of the resulting hydrogel formed by the controlled hydrolysis of tetrabutyl titanate in ethanol/acetic acid/water solution with tourmaline. The yielded tourmaline- TiO_2 nanocomposites were defined as T($x\%$)- TiO_2 , where $x\%$ referred to the mass ratio of tourmaline/ TiO_2 . The bare TiO_2 was also prepared by the same procedure above without the addition of tourmaline.

The morphologies of catalysts were examined using a LEO 1530VP field emission scanning electron microscopy (FE-SEM). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 X-ray diffractometer operated at 40 kV and 100 mA. Cu–K α radiation ($\lambda = 0.154$ nm) was employed for continuous scanning over a 2θ range of 3 – 80° with step intervals of 0.02° . Nitrogen adsorption–desorption isotherms were obtained at 77 K using an ASAP 2020/TRISTAR 3000 instrument (Micromeritics, USA). Photoluminescence (PL) spectra were recorded at room temperature on a FLS 920P Edinburgh Analytical Instrument apparatus. Photocurrent measurements were performed in a three-electrode electrochemical system (Princeton Applied Research Versa STAT 3), using a standard calomel reference electrode (SCE) and a platinum wire as a counter electrode, respectively. The chronoamperometric responses were collected in 0.5 M Na_2SO_4 electrolyte with a 1.0 V (vs. SCE) potential bias, under simulated sunlight illumination from a 150 W xenon lamp. The cell potential was controlled using a Gamry Interface 1000 potentiostat for impedance measurements and Mott–Schottky plot analyses without light illumination. Electrochemical impedance spectra (EIS) were measured at the open-circuit voltage with oscillation amplitude of 10 mV over the frequency range from 0.2 to 10^5 Hz. The interface capacitance behavior under applied potential polarization (Mott–Schottky analysis) was conducted at 100 Hz with potential steps of 50 mV.

2.3. Photocatalytic activity evaluation

Photocatalytic tests were performed in a XPA-7 photochemical reactor (Xujiang Electromechanical Plant) which is displayed in Fig.

Fig. 1. XRD patterns of the prepared catalysts. ① Tourmaline, ② TiO_2 , ③ T(2%)- TiO_2 , ④ T(5%)- TiO_2 , ⑤ T(10%)- TiO_2 , ⑥ T(20%)- TiO_2 , ⑦ T(30%)- TiO_2 .

S1 schematically, and comprises quartz test tubes, 365 nm UV cut-off filters, and a medium pressure mercury lamp ($\lambda_{\text{max}} = 365 \text{ nm}$) with illumination at 20.1 mW cm^{-2} . The light intensity distribution of mercury lamp and transparency of the cutoff filters are shown in Table S1 and Fig. S2, respectively. The reaction was maintained at ambient temperature using circulating water throughout the experiment run. Typically, before irradiation, a designated amount of photocatalyst was dispersed into 50 mL of 15 mg L^{-1} BPA solution in the quartz test tubes with magnetic stirring for 1 h to ensure an adsorption–desorption equilibrium of BPA in dark. Then the light was turned on to initiate the reaction. Samples (0.5 mL) were periodically withdrawn and centrifuged at 15,000 rpm for 5 min for HPLC quantitation of BPA. Total organic carbon (TOC) determination and GC–MS analysis for intermediate identification were performed as well. Sample pretreatment and analytical procedures were elaborated in our previous work [23]. For comparison, direct photolysis experiment was carried out without catalyst. Specific treatments were also conducted to assess the impacts of coexisting substances such as methanol, *t*-butanol and KI.

3. Results and discussion

3.1. Characterization of the catalysts

SEM micrographs of tourmaline and T(20%)- TiO_2 catalyst are presented in Fig. S3. A uniform block structure and smooth morphology could be observed on tourmaline surface, while many uniform grains emerged in T(20%)- TiO_2 catalyst, which indicated of TiO_2 deposition on the tourmaline successfully. The average size of TiO_2 agglomerates was approximately 20 nm, as estimated from the SEM micrograph.

The XRD diffractograms of tourmaline, TiO_2 and tourmaline- TiO_2 catalysts with different tourmaline contents are reflected in Fig. 1. The diffraction peaks at 2θ of 25.3° , 37.9° , 48.0° , 54.2° , 54.6° , 62.6° can be indexed to (101), (004), (200), (105), (211) and (204) reflections of anatase TiO_2 (JCPDS 21–1272), and no rutile phase appeared in the as-prepared catalysts. Besides, the additional peaks observed in tourmaline- TiO_2 composites were ascribed to the introduction of tourmaline, and the reflection intensities increased with the increase of tourmaline contents. Based on the line broadening analysis of anatase TiO_2 (101) by the Scherrer equation, the mean crystallite sizes of TiO_2 were calculated to be in the range of 8–12 nm (Table 1). In general, compared with bare TiO_2 , the addition of tourmaline increased crystallite sizes of TiO_2 within the hybrid photocatalysts.

The N_2 adsorption/desorption isotherms of the prepared catalysts showed the characteristics of type IV curve with a H2 type hysteresis loop according to the IUPAC classification (Fig. S4),

Table 1

Specific surface areas, pore volumes, pore diameters and crystal sizes of the prepared catalysts with different contents of tourmaline as the TiO_2 supports.

Catalysts	S_{BET}^a (m^2/g)	V_p^b (cm^3/g)	D_p^c (nm)	TiO_2 crystallite size ^d (nm)
TiO_2	93.0	0.15	4.7	8.2
T(2%)- TiO_2	98.2	0.13	4.3	8.8
T(5%)- TiO_2	71.9	0.08	4.1	8.5
T(10%)- TiO_2	65.5	0.08	4.3	9.8
T(20%)- TiO_2	88.1	0.11	3.9	9.2
T(30%)- TiO_2	64.9	0.07	3.8	11.5

^a Specific surface areas obtained using the multipoint BET method from adsorption data in a relative pressure P/P_0 range from 0.06 to 0.35.

^b Total pore volume (cm^3/g) at $P/P_0 = 0.99$.

^c Average pore diameters determined from the desorption branch of the isotherms by BJH method.

^d Calculated from line broadening of anatase TiO_2 (101) by the Scherrer equation.

Fig. 2. Photocatalytic degradation of BPA over tourmaline and tourmaline/ TiO_2 composite catalysts containing different tourmaline contents (catalyst dosage: 1.5 g L^{-1} ; initial BPA concentration: 15 mg L^{-1} ; pH 6.85, the same as below).

indicating pronounced mesoporosity and some degree of microporosity present in the catalysts. It was further verified from the narrow pore size distribution centered in the range of 2–6 nm (the inset of Fig. S4). The derived specific surface areas (S_{BET}), total pore volumes (V_p), and average pore diameters (D_p) are listed in Table 1. The average pore diameters varied from 3.8 to 4.7 nm. In general, the introduction of tourmaline reduced S_{BET} (except T(2%)- TiO_2), V_p , and D_p for the as-synthesized catalysts.

3.2. Photoactivity evaluation on different catalysts

Adsorption of organic compounds is often critical for photocatalysis. Figs. S5 and 2 reveal the adsorption and photocatalytic degradation of BPA over the prepared catalysts under the following conditions: catalyst dosage 1.5 g L^{-1} , BPA concentration 15 mg L^{-1} , and pH 6.85, respectively. Generally, the catalysts showed very low adsorption capacity for BPA. Except TiO_2 and T(2%)- TiO_2 , BPA removal was less than 5% by adsorption on tourmaline/ TiO_2 composites after equilibrium achieved at 60 min, corresponding to their decreased S_{BET} . During direct photolysis through 120 min UV irradiation, only 13.9% of BPA elimination was observed, and BPA decomposition photocatalyzed by tourmaline was also slow. Instead, compared with the bare TiO_2 -based system, the reaction proceeded rapidly with 2% of tourmaline incorporation, indicating the enhancement of tourmaline-involved photocatalysis. However, further increase of tourmaline contents, T(5%)- TiO_2 and T(10%)- TiO_2 did not lead to higher BPA removal rates compared to that

Fig. 3. (a) TOC removal during BPA photocatalytic decomposition over T(20%)-TiO₂ catalyst and the proposed degradation pathway. (b) BPA removal with recycle times over T(20%)-TiO₂.

in T(2%)-TiO₂ system, likely due to the reduced S_{BET} and increased crystallite sizes of T(5%)-TiO₂ and T(10%)-TiO₂. It was observed that T(20%)-TiO₂ catalyst showed higher removal rate (100%) than any of the above and the bare TiO₂ (78.9%) toward BPA degradation after 120 min UV irradiation. This enhanced photocatalytic activity arising from the introduction of tourmaline would be related to the effective separation of electron–hole pairs resulting from its strong electrostatic field. Note also that the highest removal efficiency was achieved until the optimum content (20 wt.%) of tourmaline, beyond which (30 wt.%) a slight decline of BPA degradation started to occur. One plausible explanation for this could be that excessive content of tourmaline may block the light absorption of TiO₂ to retard photocatalysis. In addition, the reduced S_{BET} for T(30%)-TiO₂ would indeed cause the reactivity decrease. In particular, T(20%)-TiO₂ exhibited much higher photoactivity than the mixture of the component phases, suggesting synergistic effect of tourmaline and TiO₂ in the as-prepared composites for photodegradation of BPA (Fig. S6).

3.3. Mineralization of BPA, intermediates and recycle tests

T(20%)-TiO₂ mediated photocatalysis could reach the efficacy of 73.3% of TOC removal after 4 h reaction with complete BPA decomposition (Fig. 3a), suggesting intermediate production during the degradation. Table S2 summarizes the information of intermediates including their molecular structure, main fragment ions (m/z) and molecular weight. Two intermediates, 2-(4-hydroxyphenyl)-2-propanol, *p*-isopropenyl phenol, were identified according to their mass spectra. A simplified degradation scheme was also proposed.

The recyclability and photoactivity of the T(20%)-TiO₂ was also investigated and tested for five cycles (Fig. 3b). Owing to the micron-sized tourmaline as support, relative convenience of

catalyst recovery could be achieved compared to that of the bare TiO₂. The results revealed only about 5% reduction of BPA removal rate after five cycles, which testified the stability of the prepared photocatalysts.

3.4. Determination of the main reactive species

Different reactive species scavengers (methanol, *t*-butanol and KI) were used to probe into the contributory roles of •OH and photogenerated holes on BPA decomposition. Methanol and *t*-butanol are commonly known as strong scavengers of •OH radicals, while KI usually acts as a trapping reagent of photogenerated holes. As displayed in Fig. 4, the presence of 0.005–0.10% (V/V) of methanol and 10–200 mM of *t*-butanol both remarkably decelerated the reaction. The inhibited effects were more distinct with the increasing addition of methanol and *t*-butanol, and BPA degradation were even completely suppressed by excess methanol and *t*-butanol, which indicated of a •OH-initiated oxidation as the dominating BPA decomposition pathway. The results were also in accordance with other TiO₂-based photocatalytic systems in previous reports [24–26]. However, 0.05 mM and 0.1 mM of KI addition exhibited insignificant effects on BPA decomposition, while the reactive rates were even accelerated in the presence of KI with higher concentrations (0.5, 1 mM). This was possibly because the hole trapping by KI resulted in electron–hole separation and high efficiency of free electrons for •OH formation [27], which in turn supported that hole oxidation was not responsible for the degradation of BPA.

3.5. Proposed mechanism

Note that tourmaline-supported TiO₂ exhibited apparently improved reactivity toward BPA degradation, and this enhance-

Fig. 4. Effects of methanol, *t*-butanol and KI on BPA photocatalytic degradation over T(20%)-TiO₂ catalyst.

Fig. 5. (a) Photoluminescence spectra at room temperature. (b) Chronoamperometric responses recorded at 1.0 V vs. SCE for the prepared photocatalysts. (c) EIS for the prepared photocatalysts as was recorded under a DC bias of open circuit potential and presented in the Bode form. (d) Mott-Schottky plots and the calculated carrier densities obtained from the corresponding slopes for the prepared photocatalysts in dark.

ment was not correlated to the S_{BET} , the crystallite size and BPA adsorption capacity in comparison with bare TiO₂. Given that charge separation, transfer, and carrier lifetime play important roles in a photocatalysis process, photoluminescence (PL) emission spectrum was employed to evaluate the fate of charge carriers. The PL spectrum for all samples comprise broad luminescence bands (Fig. 5a), which would be ascribed to the radiative recombination of self-trapped excitons [28]. Peak shifts are often resulted from the electron trapping before recombination [29]. The PL results clearly revealed the efficient charge transfer of the het-

ero samples with increasing tourmaline content, corresponding to the emission decay profiles. The enhanced electron shuttling efficiency of tourmaline was further corroborated with photocurrent measurements. The transient photocurrent responses were collected for light on-off cycles under simulated sunlight illumination (Fig. 5b). The photocatalysts displayed prompt, reproducible photocurrent responses upon illumination cycles, and no distinct current decay occurred, which indicated the certain stability of the catalysts. As expected, no obvious current was detected for tourmaline alone, while the introduction of tourmaline greatly increased

Fig. 6. Schematic diagrams reflecting the energy levels associated with band bending of TiO₂ semiconductor for (a) the bare TiO₂ and (b, c) the tourmaline/TiO₂ composites with opposite polarization directions, and (d) the transport of photogenerated electrons and holes. E_c , E_f , E_v are the energies of the conduction band, Fermi level and valence band, respectively.

the photocurrent generation for TiO₂. Compared to the bare TiO₂, the photocurrent density promotion from 2.9 to 8.0 $\mu\text{A cm}^{-2}$ could be achieved. The outcome confirmed the facilitated migration of charge carriers and higher photon-to-electron conversion efficiency in tourmaline/TiO₂-based heterogeneous photocatalysis, which was responsible for the superior photocatalytic reactivity.

To validate our postulation that lowered carrier recombination contributed to the activity improvement, electrochemical impedance spectra (EIS) were measured to investigate the bulk and/or surface recombination and charge transfer properties, as presented in Bode plots in Fig. 5c. Compared to the EIS of the bare TiO₂, noticeable difference could be observed on the interface electron-transfer resistance with tourmaline incorporation. The obvious decreased impedance of tourmaline/TiO₂ hetero photocatalysts indicated a low charge-transfer resistance and thus, a reduction of recombination losses, which are beneficial to the photocatalytic process. In addition, Mott–Schottky analyses were conducted to gain further insight into the charge transfer properties. The Mott–Schottky property was in line with the expected behavior of n-type semiconductor for the obtained positive slope. Noticeably, tourmaline/TiO₂ composites showed much lower slopes compared to the bare TiO₂, indicating an increased charge carrier concentration. Carrier densities (N_d) of the prepared photocatalysts were estimated based on the corresponding slopes

of Mott–Schottky plots near the flat band potential according to following equation:

$$N_d = \frac{2/e_0\epsilon\epsilon_0}{d(1/C^2)/dV}$$

where e_0 is the electron charge (1.6×10^{-19} C), ϵ the relative permittivity of TiO₂ (30 for anatase [30]), ϵ_0 the permittivity of vacuum (8.86×10^{-14} F cm⁻¹), C is the capacitance derived from the electrochemical impedance at different potential (V). It should be noted the calculated carrier density (shown in Fig. 5d) was improved by about one order of magnitude with tourmaline incorporation, which significantly enhanced the conductivity, and further contributed to the charge transfer and photocurrent generation. Although the exact value of the calculated carrier density (N_d) from Mott–Schottky plot is semi-quantitative and may suffer from inaccuracies [30–32], the improved carrier concentration for tourmaline/TiO₂ composites was evident based on qualitative comparison of the slopes.

Photocatalytic capability is also predominated by the band energy positions of the photocatalyst, which in fact reflect the reduction potential of electrons, the oxidizing ability of holes and, thereby, the potential to initiate redox reactions [3]. As such, energy levels associated with band bending in the photocatalysts were evaluated, as shown schematically in Fig. 6, with the aim to inves-

tigate the effects of tourmaline on the surface electronic structures of CB and VB in the TiO_2 semiconductor (with the assumed band gap of 3.2 eV) and the transport of charge carriers. It is assumed that the potential of free electrons in the TiO_2 semiconductor, namely, the Fermi energy E_F , is higher compared to the redox potential of reaction solution $E_{F,\text{redox}}$. To establish an electrochemical potential equilibrium across the two phases, electron shuttling preferentially directed from the semiconductor to the solution occurs until E_F , $E_{F,\text{redox}}$ equilibrate, which creates a region with excess ionized donors (mainly oxygen vacancies for TiO_2) [33] and positive charges below the surface, commonly known as the space charge region, and a negative charge layer at the solution/solid interface. Because of the electron depletion from the semiconductor, the space charge region is also called as the depletion layer in this scenario. As a consequence, the charge carrier redistribution causes the electronic structure differences between the depletion layer and the bulk of semiconductor, and spatially varied energy levels of the bands, which is referred to as band bending. Due to the formed electron-rich layer at the interface, resulting in the higher potential of the electrons at the surface than the bulk, the conduction and valence bands bend upward (Fig. 6a) [34], and a potential barrier is built similar to the Schottky potential barrier, which will block further transport of electrons to the solution. Meanwhile, an internal electric field also exists across the space charge region.

The spatial degree of band bending usually depends on the electronic structure of semiconductor and space charge potential, and affects remarkably the transfer of charge carriers [34]. The incorporating of tourmaline will change the band bending of TiO_2 semiconductor and, thereby, will assist the charge separation, transfer and lengthen the lifetime of charge carriers, due to the internal dipolar field present resulting from the spontaneous polarization. Spontaneous polarization originates from replacements of individual atoms or ions in the lattice sites, with the positive and negative charges occupying in different symcenters. In an optimized scenario, we assume the polarization vectors are along the directions oriented perpendicular to the solution/semiconductor interface. For the case in Fig. 6b, where the internal dipolar field arising from the spontaneous polarization of tourmaline is directed toward the semiconductor surface, further depletion of electrons from the space charge region occurs. This leads to a greater potential of electrons at the solution/ TiO_2 interface and the increased band bending upward, in comparison with the scenario displayed in Fig. 6a. Photogenerated holes will readily drift to the surface to initiate the reaction, while photoelectrons transfer is limited. The opposite process will occur for the case in Fig. 6c. On this occasion, the space charge region experiences a potential decline and the band bending is reduced. Even downward band bending and accumulation layer can be presented, depending on the surface potential and polarization potential. This enables photoexcited electrons effectively diffuse to the surface for participation in the reduction reaction. The separated electrons and holes can be then involved in the generation of reactive species (Fig. 6d). Specifically, the trapped holes react with $\text{OH}^-/\text{H}_2\text{O}$ to give rise to highly reactive $\bullet\text{OH}$. Meanwhile, electrons can be trapped by adsorbed O_2 to form $\text{O}_2^{\bullet-}$, which may be converted into $\text{HO}_2^{\bullet}$, H_2O_2 via further reaction. H_2O_2 serves as a direct source of $\bullet\text{OH}$, either by homolytic scission or by capturing of an electron. The formed $\bullet\text{OH}$ is mainly responsible for BPA decomposition. Furthermore, it has been implied that micronscale ferroelectric core will preferably provide full extended polarization and band bending [15], and polarization orientations can be differed in each domain of ferroelectric, that is, different spatial degree of band bending will occur at distinct surface regions. Similar to this, the incorporation of micron-sized tourmaline will consequently ensure high efficiencies for electron–hole separation, spatially selective redox reaction and, therefore, limited back-reaction at different surface locations. This has been also

verified by spatially separated redox products yielded on TiO_2 film supported on BaTiO_3 [14]. Thus, the tourmaline-supported TiO_2 , with the synergistic functions between internal dipolar field and photoreactivity, offers a promising approach, spontaneous polarization assisted photocatalysis, which contributes to the enhanced degradation of BPA.

3.6. Implications for future research

The synergy between tourmaline and TiO_2 on photoactivity could merit tourmaline, a polar mineral, as a promising candidate for incorporation with TiO_2 , based on its functional properties in terms of the presence of internal dipolar field arising from the spontaneous polarization. The results indeed revealed the underlying benefits associated with the utilization of earth-abundant tourmaline as supports for TiO_2 -based photocatalyst, which would be meaningful for development of nanotechnology enabled approaches in cost-effective environmental application. It should be noted that the enhanced effect was also observed for photoreductive debromination of tetrabromobisphenol A with different structure and properties from BPA (unpublished work). Considering the significant promotion of transient photocurrent responses from tourmaline incorporation (Fig. 5b), further superior photocatalytic reactivity would be anticipated under simulated sunlight illumination, and the corresponding study is in progress. Although the exact value of internal electric field was not determined and further exploration is needed regarding the exact responsible mechanism, the concept of utilizing a natural mineral with low cost to approach the goal of spontaneous polarization assisted photocatalysis can indeed shed new light on applied environmental catalysis and addressing the limitation of quantum efficiency for application of semiconductor.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2015.10.006>.

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